#18 2/20/03

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application No.:	09/775,106
Filing Date:	February 1, 2001
Applicant:	Mourou
Group Art Unit:	1725
Examiner:	G. Evans
Title:	METHOD FOR CONTROLLING CONFIGURATION OF LASER INDUCED BREAKDOWN AND ABLATION
Attorney Docket:	2115D-000939/DVC

Commissioner of Patents and Trademarks
Washington, D.C. 20231

DECLARATION UNDER 37 CFR 1.131

The undersigned hereby declare that:

1. We are the inventors of the subject matter described and claimed in the above identified patent application, serial no. 09/775,106 which is a divisional of reissue application serial no. 366,685, which is a reissue application of patent no 5,656,186 filed April 8, 1994, as Serial No. 08/224,961.

2. Prior to March 31, 1994, invention disclosure materials concerning the subject matter of the above identified patent application were submitted to the

Technology Management Office of the University of Michigan and to its outside counsel, Linda Deschere. Such invention disclosure materials included, but were not limited to, the documents contained in Exhibit 1 attached hereto. Such documents are entitled a) Sub-Wavelength Micro-Machining by Ultrafast Laser Ablation; b) Laser-Induced Breakdown by Impact Ionization in SiO_2 with Pulse-widths from 7 ns to 150 fs; and c) Damage Threshold as a Function of Pulse Duration in Biological Tissue. The materials of Exhibit 1 were not published prior to filing of the Application Serial No. 08/224,961.

3. It is our understanding that prior to March 31, 1994, the Technology Management Office of the University of Michigan requested that attorney Linda Deschere prepare a patent application based on the invention disclosure.

4. It is our understanding that attorney, Linda Deschere prepared a draft of the above identified patent application at least as early as March 31, 1994. On Thursday, March 31, 1994, Linda Deschere sent such draft patent application via facsimile to Mitchell A. Goodkin which was forwarded to us for review. A copy of the letter dated March 31, 1994 transmitting the draft patent application is attached as Exhibit 2.

5. At least as early as March 31, 1994, at least a set of claims for the draft of the above identified patent application was sent to inventor, Peter Pronko. On Thursday, March 31, 1994, Peter Pronko sent his comments regarding the claims for

the patent application to Linda Deschere. A copy of the facsimile cover transmitting Mr. Pronko's comments is attached as Exhibit 3.

6. On Tuesday, April 5, 1994, inventors, Jeff Squier and Gerard Mourou, sent their comments regarding the draft patent application of March 31, 1994 to Linda Deschere. A copy of the facsimile cover transmitting comments of Jeff Squier and Gerard Mourou is attached as Exhibit 4.

7. It is our understanding that Linda Deschere prepared a subsequent draft patent application based on our comments regarding the earlier draft patent application. On Wednesday, April 6, 1994, Linda Deschere sent the subsequent draft patent application via facsimile for our review. A copy of the letter transmitting the subsequent draft patent application is attached as Exhibit 5.

8. On Thursday, April 7, Gerard Mourou sent a facsimile transmission to Linda Deschere containing corrections to the draft of Exhibit 5. A copy of the facsimile cover transmitting such corrections is attached as Exhibit 6.

9. The above identified patent application was filed with the United States Patent and Trademark Office on Friday, April 8, 1994.

10. The letters and faxes including the attachments referenced therein have been maintained in confidence. As such, we, the inventors, hereby expressly reserve and do not waive, directly or indirectly, our rights and protection under the attorney-client privilege and work product doctrine in all communications with our attorneys which communications accompanied the letters and fax cover sheets referred to and attached to this declaration, whereby the submission of the transmittals herewith does not constitute a waiver of such rights and protection.

11. The undersigned acknowledge that willful false statements and the like are punishable by fine or imprisonment, or both (18 USC 1001) and may jeopardize the validity of the application or any patent issuing thereon. The undersigned declares that all statements made of the declarant's own knowledge are true and that all statements made on information and belief are believed to be true.

Gerard Mourou	Date	Paul Lichter	Date
Detao Du	Date	Xinbing Liu	Date
Subrata Dutta	Date	Peter Pronko	Date
[signature] Victor Elner	1/3/03 Date	Jeffrey Squier	Date
Ron Kurtz	Date		

LIST OF EXHIBITS

Exhibit 1	a)	Sub-Wavelength Micro-Machining by Ultrafast Laser Ablation;
	b)	Laser-Induced Breakdown by Impact Ionization in SiO_2 with Pulse-widths from 7 ns to 150 fs; and
	c)	Damage Threshold as a Function of Pulse Duration in Biological Tissue.
Exhibit 2		Copy of letter dated March 31, 1994 from Linda Deschere transmitting a draft patent application
Exhibit 3		Copy of the facsimile cover dated March 31, 1994 from Peter Pronko to Linda Deschere transmitting inventor, Peter Pronko's comments
Exhibit 4		Copy of the facsimile cover dated April 5, 1994 from Jeff Squier and Gerard Mourou to Linda Deschere transmitting comments of inventors, Jeff Squier and Gerard Mourou
Exhibit 5		Copy of the letter dated April 6, 1994 from Linda Deschere transmitting a subsequent draft patent application
Exhibit 6		Copy of facsimile cover dated April 7, 1994 from Gerard Mourou to Linda Deschere transmitting comments

EXHIBIT 1(a)

USSN 09/775,106

Sub-Wavelength Micro-Machining by Ultrafast Laser Ablation

S. K. Dutta, P. P. Pronko, and G. Mourou
Center for Ultrafast Optical Science
Dept. of Electrical Engineering
and Computer Science
University of Michigan
Ann Arbor, MI 48109
313-763-4875

Introduction

Current laser machining using nano-second pulses cannot produce features smaller than the spot size due to thermal interactions with the material [1]. This paper presents arguments and a demonstration that by using femtosecond pulses the spatial resolution of the ablation/machining process can be considerably less than the wavelength of the laser radiation used to produce it. We have produced laser ablated holes with diameters of 10% the laser beam spot size.

Theory

The basic premise for explaining our observations is found in (a) the solid state thermal diffusion length for the deposited optical energy, (b) the absorption depth for the optical radiation and (c) the time necessary for a vapor to develop at the surface of the material.

For ultrafast pulses in metals the thermal diffusion length, $l_{th}=(Dt)^{1/2}$ (where D is the thermal diffusivity and t the pulse time), is significantly smaller than the absorption depth (1/a), where a is the absorption coefficient for the radiation. For our experimental conditions with wavelength of 800 nm and 200 fs pulses on gold, the absorption depth is 275 A with a diffusion length of 50 A. In the case of nanosecond pulses the diffusion length, which is on the order of 10 μm, is much longer than the absorption depth, resulting in thermal diffusion being the limiting factor in feature size resolution. Empirical evidence for the existence of these two regimes is exhibited in Figure 1. Here, both experimental [2] and theoretical [3] ablation thresholds are plotted as a function of pulse width. An arrow at approximately 7 picoseconds delineates the point at which the thermal diffusion length (l_{th}) is equal to the absorption depth (1/a). It is clear from the figure that this is the point at which the ablation threshold transitions from a slowly varying or nearly constant value as a function of pulse width to one that is dramatically dependent on pulse time. In further support of these arguments, it has been demonstrated [4] that the electron thermalization time for laser deposited energy in gold is on the order of, or less than, 500 fs and the electron-lattice interaction time is 1 ps.

The consequences of this for ultrafast laser pulses is that the energy is contained within the beam spot. In fact for energies at or near the threshold for ablation, the spatial profile of the laser beam will determine the size and shape of the region being ablated.

We have performed an experiment to measure the amount of recombination light produced as a function of the fluence impinging on a gold film. The technique involved is explained in detail in a similar study based on transparent materials [5]. We take the intensity of the light to be proportional to the amount of material ablated. In Figure 2, the material removed is plotted as a function of fluence. A well defined threshold fluence is observed at which material removal is initiated. It is expected that by having only a small fraction of the gaussian beam where the fluence is greater than the threshold, the ablated region can be restricted to this small area. In Figure 2, R_a is the radial position on the beam where the fluence is at threshold. Ablation, then, occurs only within a radius R_a. It

is evident that by properly choosing the incident fluence, the ablated spot can in principle be smaller than the spot size, R_S. Although the data for a 150 fs pulse is shown, this threshold behavior is exhibited in a wide range of pulse widths. However, sub spot size ablation is not possible in the longer pulse regimes, due to the dominance of thermal diffusion.

Experiment

Our laser source is a 800 nm Ti:Sapphire oscillator whose pulses are stretched by a grating pair, amplified in a regenerative amplifier operating at 1 kHz, and finally recompressed by another grating pair. We can obtain pulse widths from 7 ns to 100 fs. The beam is focused with a 10x objective, implying a theoretical spot size of 3.0 μm. Figure 3 shows an SEM photo-micrograph of ablated holes obtained in a silver film on glass, using a pulse width of 200 fs and a pulse energy of 30 nJ (fluence of 0.4 J/ cm^2). Two holes of diameter approximately 0.3 μm are clearly visible. Similar results have been obtained in aluminum.

These results suggest that by, producing a smaller spot size which is a function of numerical aperture and wavelength, even smaller holes can be machined. We have demonstrated the ability to generate the fourth harmonic (200 nm) using a nonlinear crystal. Thus by using a stronger objective lens along with the 200 nm light, holes with diameters of 200 angstroms could in principle be formed.

Conclusion

It has been demonstrated that sub-wavelength holes can be machined into metal surfaces using femtosecond laser pulses. The effect is physically understood in terms of the thermal diffusion length, over the time period of the pulse deposition, being less than the absorption depth of the incident radiation. The interpretation is further based on the hole diameter being determined by the lateral gaussian distribution of the pulse in relation to the threshold for vaporization and ablation.

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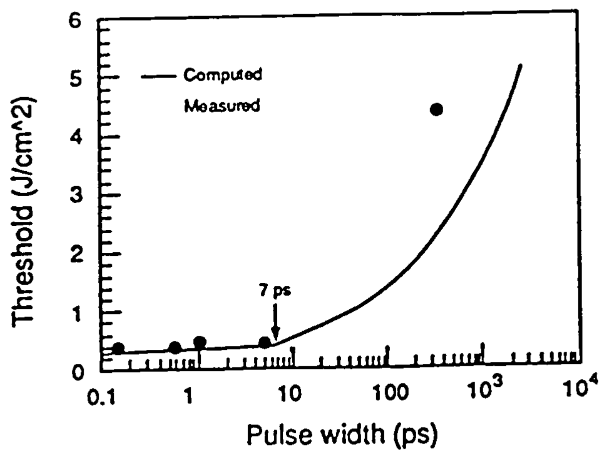

Figure 1. Ablation threshold vs. pulsewidth in gold.

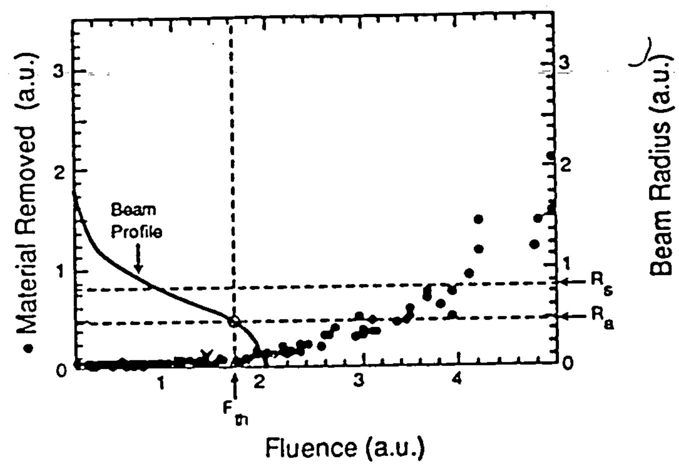

Figure 2. Sub spot size machining at ablation threshold in gold.
Fth is the threshold fluence needed to initiate material removal.
Rs is the spot size of the incident beam and Ra is the radius of the ablated hole.

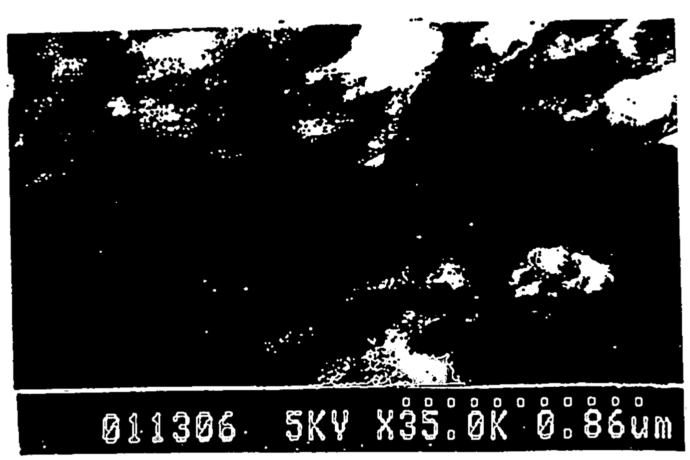

Figure 3. SEM view of two 0.3 μm holes machined in silver film.

Laser-Induced Breakdown by Impact Ionization in SiO_2 with Pulse-widths from 7 ns to 150 fs

D. Du, X. Liu, G. Korn, J. Squier, and G. Mourou

Center for Ultrafast Optical Science, University of Michigan, Ann Arbor, MI 48109-2099

Abstract

Results of laser-induced breakdown experiments in fused silica (SiO_2) employing 150 fs – 7 ns, 780 nm laser pulses are reported. The avalanche ionization mechanism is found to dominate over the entire pulse-width range. Fluence breakdown threshold does not follow the scaling of $F_{th} \sim \sqrt{\tau_p}$, when pulses are shorter than 10 ps. The impact ionization coefficient of SiO_2 is measured up to $\sim 3 \times 10^8$ V/cm. The relative role of photoionization in breakdown for ultrashort pulses is discussed.

Typeset using REVTEX

Laser-induced breakdown (LIB) in optically transparent materials has been studied extensively since the laser was invented in the 1960's [1]– [4]. LIB mechanisms have been investigated for laser pulse-widths down to tens of picoseconds. LIB remains an important topic because of its role in a wide range of high-power laser applications, where damage to optical components due to LIB often is the ultimate restriction on system performance. Increasingly, high laser power is achieved with moderate amount of energy ($\sim$ joules) by reducing the pulse-width from picoseconds to femtoseconds. Our present work is to investigate LIB in this important regime.

It is a well-established fact that the breakdown threshold depends on the pulse-width of the laser pulses. An empirical scaling law of the fluence breakdown threshold for longer pulses ($\tau_p > 30$ ps) exists [6]: $F_{\rm th} \propto \sqrt{\tau_p}$. Until recently, the shortest pulses available for LIB studies were in the range of tens of picoseconds. However, new techniques in ultrashort laser pulse generation and amplification, such as the chirped-pulse amplification (CPA) [7], have pushed the available pulse-widths to femtosecond regime. More importantly, CPA readily allows one to vary the laser pulse-width continuously — up to hundreds of picoseconds — from a single laser system based on this principle. The setup of an LIB experiment using such a laser can therefore have a wide range of laser pulse-widths, without changing other important parameters, such as the focusing of the pulse onto the sample.

We have performed a series of experiments to determine the LIB threshold as a function of laser pulse-width between 150 fs – 7 ns, using a CPA laser system. The short-pulse laser used in our experiment was a 10-Hz Ti:sapphire oscillator-amplifier system based on the CPA technique. The laser pulse was focused by an $f = 25$ cm lens inside the SiO_2 sample. The Rayleigh length of the focused beam is ~ 2 mm. The focused spot-size was measured in-situ by a microscope objective lens. The measured spot-size (FWHM) was 26 μm in a gaussian mode. The fused silica samples were made from Corning 7940, with a thickness of 0.15 mm. They were optically polished on both sides with a scratch/dig of 20-10. Each sample was cleaned by methanol before the experiment. Thin samples were used in order to avoid the complications of self-focusing of the laser pulses in the bulk. The SiO_2 sample

was mounted on a computer-controlled motorized X-Y translation stage. Each location on the sample was illuminated by the laser only once.

Two diagnostics were used to determine the breakdown threshold $F_{\rm th}$. First, the plasma emission from the focal region was collected by a lens to a photomultiplier tube with appropriate filters. Second, the change of transmission through the sample was measured with an energy meter. Visual inspection was performed to confirm the breakdown at nanosecond pulse duration. Fig. 1 shows typical plasma emission and transmitted light signal vs. incident laser energy plots, at a laser pulse-width of τ_p = 300 fs. It is worth noting that the transmission changed slowly at around $F_{\rm th}$. This can be explained by the the temporal and spatial behavior of the breakdown with ultrashort pulses. Due to the spatial variation of the intensity, the breakdown will reach threshold at the center of the focus, and because of the short pulse duration, the generated plasma will stay localized. The decrease in transmitted light is due to the reflection, scattering, and absorption by the plasma. By assuming a gaussian profile in both time and space for the laser intensity, and further assuming that the avalanche takes the entire pulse duration to reach threshold, one can show that the transmitted laser energy U_t as a function of the input energy U is given by

$$U_t = \begin{cases} kU, & U \leq U_{th} \\ kU_{th}\left[1 + \ln\left(U/U_{th}\right)\right], & U > U_{th} \end{cases} \tag{1}$$

where k is the linear transmission coefficient. The solid curve in Fig. 1 is plotted using Eq. (1), with U_{th} as a fitting parameter. In contrast, breakdown caused by nanosecond laser pulses cuts off the transmitted beam near the peak of the pulses [8], indicating a different temporal and spatial behavior.

Figure 2 shows the fluence breakdown threshold $F_{\rm th}$ as a function of laser pulse-width. From 7 ns to about 10 ps, the breakdown threshold follows the scaling law of $F_{\rm th} \propto \sqrt{\tau_p}$. Breakdown thresholds from earlier work in this pulse width regime are also shown as a comparison – it can be seen that our data is consistent with earlier work. However, when the pulse-width becomes shorter than a few picoseconds, the threshold starts to increase. This increase at shorter pulse-widths may come as a surprise at first, but it still falls into

the regime of an avalanche dominated process at high field strength, as we will show below.

The ionization process of a solid illuminated by an intense laser pulse can be described by the general equation

$$\frac{dn_e(t)}{dt} = \eta(E)n_e(t) + \left(\frac{dn_e(t)}{dt}\right)_{\mathrm{PI}} - \left(\frac{dn_e(t)}{dt}\right)_{\mathrm{loss}}, \tag{2}$$

where $n_e(t)$ is the free electron (plasma) density, $\eta(E)$ is the avalanche coefficient, and E is the electric field strength. The second term on the right hand side is the photoionization contribution, and the third term is the loss due to electron diffusion, recombination, etc. When the pulse-width is in the picosecond regime, the loss of the electron is negligible during the duration of the short pulse.

Photoionization contribution can be estimated by the tunneling rate [9]. For short pulses, $E \sim 10^8$ V/cm, the tunneling rate is estimated to be $w \sim 4 \times 10^9$ sec^{-1}, which is small compared to that of avalanche, which is derived below. However, photoionization can provide the initial electrons needed for the avalanche processes at short pulse-widths. For example, our data shows at 1 ps, the rms field threshold is about 5×10^7 V/cm. The field will reach a value of 3.5×10^7 V/cm (rms) at 0.5 ps before the peak of the pulse, and $w \sim 100$ sec^{-1}. During a $\Delta t \sim 100$ fs period the electron density can reach $n_e \sim n_t[1 - \exp(-w\Delta t)] \sim 10^{11}$ cm^{-3}, where $n_t \sim 10^{22}$ is the total initial valence band electron density.

Neglecting the last two terms in Eq. (2), we then have the case of an electron avalanche process, with impact ionization by primary electrons driven by the laser field. The electron density is then given by $n_e(t) = n_0 \times \exp(\eta(E)t)$, where n_0 is the initial free electron density. These initial electrons may be generated through thermal ionization of shallow traps or photoionization. When assisted by photoionization at short pulse regime, the breakdown is more deterministic, as contrary to that of nanosecond pulses, where the breakdown is more statistical [10]. According to the commonly accepted condition that breakdown occurs when the electron density exceeds $n_{th} \simeq 10^{18}$ cm^{-3} and an initial density of $n_0 \simeq 10^{10}$ cm^{-3}, the breakdown condition is then given by $\eta\tau_p \simeq 18$ [5], [10]. For our experiment, it is more appropriate to use $n_{\mathrm{th}} \simeq 1.6 \times 10^{21}$ cm^{-3}, the plasma critical density, hence the threshold

is reached when $\eta\tau_p \simeq 30$. There is some arbitrariness in the definition of plasma density relating to the breakdown threshold. However, the particular choice of plasma density does not change the dependence of threshold as function of pulse duration (the scaling law).

In our experiment, the applied electric field is on the order of a few tens of MV/cm and higher. Under such a high field, the electrons have an average energy of $\sim$ 5 eV, and the electron collision time τ is less than 0.4 fs for electrons with energy $U \geq 5-6$ eV [11]. Electrons will make more than one collision during one period of the electric oscillation. Hence the electric field is essentially a dc field to those high energy electrons. The breakdown field at optical frequencies has been shown to correspond to dc breakdown field by the relationship [2] $E_{\mathrm{th}}^{\mathrm{rms}}(\omega) = E_{\mathrm{th}}^{\mathrm{dc}}(1+\omega^2\tau^2)^{1/2}$, where ω is the optical frequency and τ is the collision time.

In dc breakdown, the ionization rate per unit length, α, is used to describe the avalanche process, with $\eta = \alpha(E)v_{\mathrm{drift}}$, where v_{drift} is the drift velocity of electrons. When the electric field is as high as a few MV/cm, the drift velocity of free electrons is saturated and independent of the laser electric field, $v_{\mathrm{drift}} \simeq 2 \times 10^7$ cm/s [12].

Thornber [13] has derived an expression for $\alpha(E)$ which is applicable for all electric field strengths, which is essential when comparing to our experimental data. The ionization rate per unit length of an electron is just eE/U_i times the probability, $P(E)$, that the electron has an energy $\geq U_i$, or $\alpha(E) = (eE/U_i)P(E)$. We denote $E_{kT}, E_p,$ and E_i as threshold fields for electrons to overcome the decelerating effects of thermal, phonon, and ionization scattering, respectively. When the electric field is negligible, $E < E_{kT}$, so the distribution is essentially thermal, $P(E)$ is simply $\exp(-U_i/kT)$. Shockley [14] showed $P(E) \sim \exp(-\mathrm{const}/E)$ for $E_{kT} < E < E_p$. Wolff [15] found $P(E) \sim \exp(-\mathrm{const}/E^2)$ at higher fields ($E > E_p$). Thornber combined the three cases and gave an expression that satisfies both low and high field limits:

$$\alpha(E) = \frac{eE}{U_i} \exp\left(-\frac{E_i}{E(1+E/E_p)+E_{kT}}\right). \tag{3}$$

This leads to $F_{\mathrm{th}} \propto E^2\tau_p \sim 1/\tau_p$, i.e., the fluence threshold will increase for ultrashort laser

pulses when $E > \sqrt{E_p E_i}$ is satisfied.

In Fig. 3, we plot α as a function of the electric field, E. From our experimental data, we calculate α according to $\eta\tau_p = 30$ and $\eta = \alpha v_{\rm drift}$. The solid curve is calculated from Eq. (3), using $E_i = 30$ MV/cm, $E_p = 3.2$ MV/cm, and $E_{kT} = 0.01$ MV/cm. These parameters are calculated from $U = eEl$, where U is the appropriate thermal, phonon, and ionization energy, and l is the corresponding energy relaxation length ($l_{kT} = l_p \sim 5$ Å, the atomic spacing, and $l_i \simeq 30$ Å, see [16] and the references there in). It shows the same saturation as the experimental data. The dashed line is corrected by a factor of 1.7, which results in an excellent fit with the experimental data. This factor of 1.7 is of relatively minor importance, as it can be due to a systematic correction, or because breakdown occurred on the surface first, which could have a lower threshold. The uncertainty of the saturation value of $v_{\rm drift}$ also can be a factor. The most important aspect is that the shape (slope) of the curve given by Eq. (3) provides excellent agreement with the experimental data. This prompts us to conclude that in our experiments, the mechanism of laser-induced breakdown in fused silica, using pulses as short as 150 fs and wavelength at 780 nm, is still dominated by the avalanche process.

In summary, we have investigated the pulse-width dependence of the laser-induced optical breakdown threshold in fused silica with laser pulse-widths over approximately 5 orders of magnitude, from 7 ns to 150 fs. We are able to obtain very good agreement, over the entire pulse-width range, on the ionization rate α between experiment and impact ionization theory. For picosecond pulses, evidence shows that photoionization is responsible for the initial electron generation. The plasma generated during breakdown with ultrashort pulses remains localized at the threshold, which could provide precise control of the interaction region for material processing and medical laser applications when ultrashort pulses are used. Our study is also relevant to solid-state microelectronics, as the structures become smaller and faster, electron transport properties under high fields and short durations – conditions explored in our experiment – will be increasingly important.

This work was funded by the Office of Naval Research and the National Science Foundation through the Center for Ultrafast Optical Science under STC PHY 8920108. We wish to thank T. Norris for helpful comments and P. Schermerhorn of Corning, Inc., who provided fused silica samples for the experiment.

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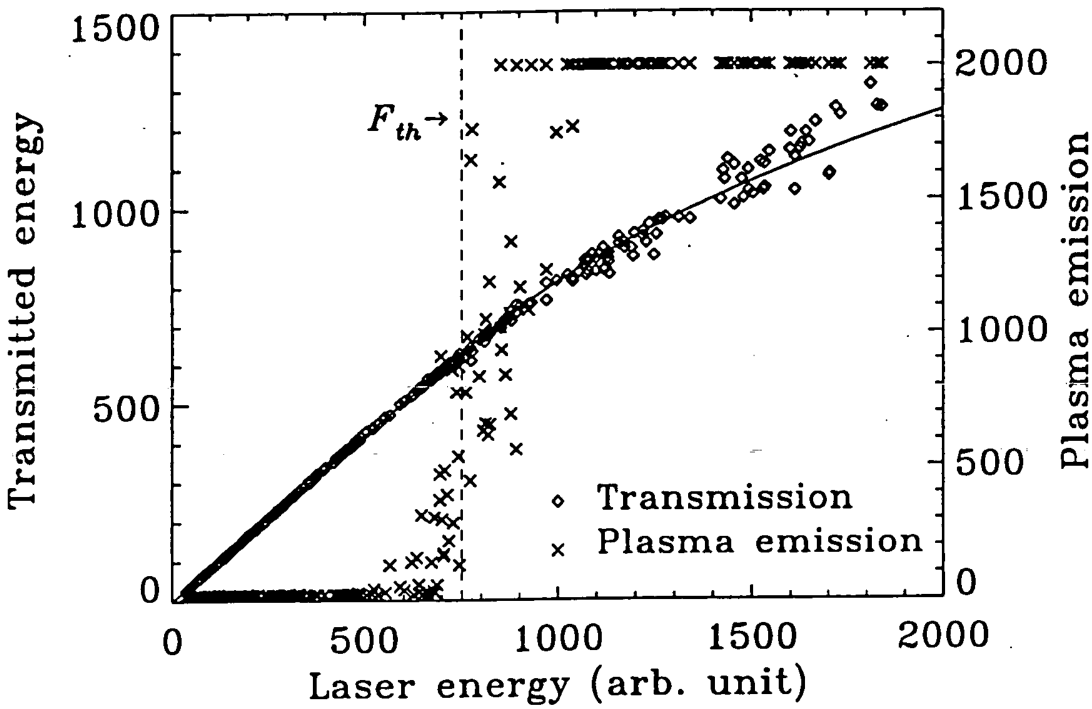
FIGURES


1500
1000
500
0
Transmitted energy
2000
1500
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Plasma emission
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× Plasma emission
0
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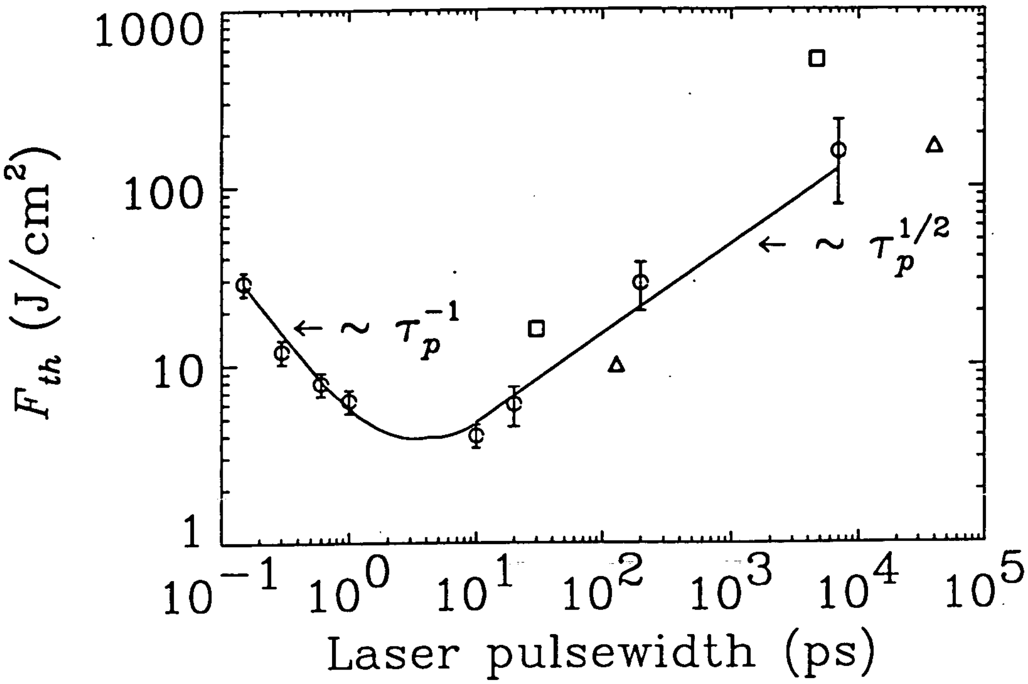
1000
1500
2000
Laser energy (arb. unit)


1000
100
10
1
F_{th} (J/cm^2)
$\leftarrow \sim \tau_p^{-1}$
$\leftarrow \sim \tau_p^{1/2}$
10^{-1} 10^0 10^1 10^2 10^3 10^4 10^5
Laser pulsewidth (ps)

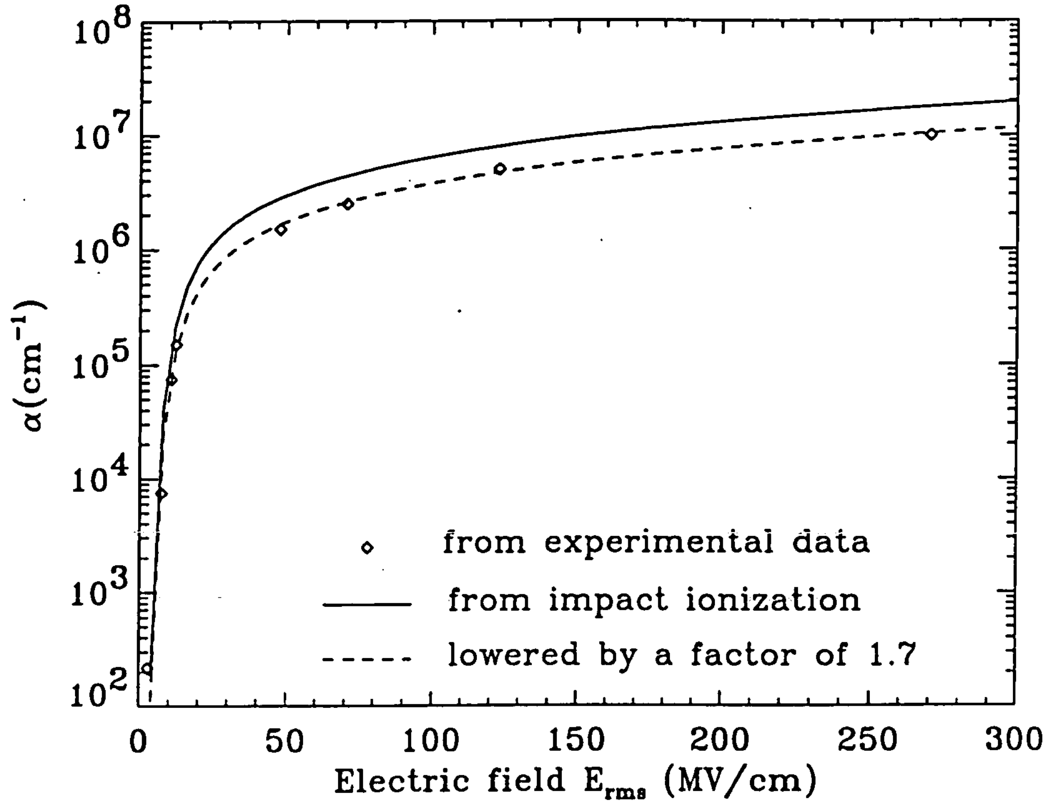

10^8
10^7
10^6
10^5
10^4
10^3
10^2
$\alpha(cm^{-1})$
0
50
100
150
200
250
300
Electric field E_{rms} (MV/cm)
from experimental data
from impact ionization
lowered by a factor of 1.7

Figure Captions

FIG. 1. Scattered plasma emission and transmitted laser pulse as a function of incident laser pulse energy.

FIG. 2. Fluence threshold vs. pulse-width. The $\sqrt{\tau_p}$ scaling holds for pulse-widths down to 10 ps, shown by the solid line. For longer pulse-widths, previously obtained bulk (squares, Smith [3]) and surface (triangles, Stokowski *et al.* [17]) damage data are also shown.

FIG. 3. Impact ionization rate per unit distance α determined from experiment and theory.

Damage Threshold as a Function of Pulse Duration in Biological Tissue

Detao Du, Jeff Squier, Xinbing Liu, Gerard Mourou
Center for Ultrafast Optical Science
University of Michigan.
2200 Bonisteel, IST Bldg. Rm. 1006
Ann Arbor, MI 48109-2099
Ph:(313) 763-4875 Fax: (313) 763-4876

Geoff Güttmann
Center for Ultrafast Optical Science
University of Michigan.
2200 Bonisteel, IST Bldg. Rm. 1006
Ann Arbor, MI 48109-2099
and
Department of Ophthalmology
Kellogg Eye Center
University of Michigan
1000 Wall Street
Ann, Arbor MI 48105

Ron Kurtz, Victor Elner
Department of Ophthalmology
Kellogg Eye Center
University of Michigan
1000 Wall Street
Ann, Arbor MI 48105

Abstract

Damage thresholds for corneal tissue are measured as a function of pulse duration, revealing strong departure from previous findings.

Damage Threshold as a Function of Pulse Duration in Biological Tissue

Detao Du, Jeff Squier, Xinbing Liu, Gerard Mourou
Center for Ultrafast Optical Science
University of Michigan.
2200 Bonisteel , IST Bldg. Rm. 1006
Ann Arbor, MI 48109-2099
Ph:(313) 763-4875 Fax: (313) 763-4876

Geoff Güttmann
Center for Ultrafast Optical Science
University of Michigan.
2200 Bonisteel , IST Bldg. Rm. 1006
Ann Arbor, MI 48109-2099
and
Department of Ophthalmology
Kellogg Eye Center
University of Michigan
1000 Wall Street
Ann, Arbor MI 48105

Ron Kurtz, Victor Elner
Department of Ophthalmology
Kellogg Eye Center
University of Michigan
1000 Wall Street
Ann, Arbor MI 48105

Summary

We measured damage thresholds for corneal tissue over a range of pulse durations (from 150 fs - 7 ns) that could not be examined previously with a single laser source, using a Ti:sapphire chirped-pulse amplification (CPA) laser [1]. Our results depart from previous findings [2,3], which had to use multiple laser sources to investigate a similar pulsewidth range.

For ultrashort pulse durations (<10 ps), the primary mechanisms for tissue damage have not been described. For certain applications, such as ophthalmic surgery, collateral damage must be minimized. By understanding the mechanisms and defining the breakdown thresholds for ultrashort pulse durations, we hope to reduce collateral damage for these precision applications.

Laser-induced optical breakdown consists of three general steps: free electron generation and multiplication, plasma heating and material deformation or breakdown. Avalanche ionization and multiphoton ionization are the two processes responsible for the breakdown. The laser-induced breakdown threshold in dielectric material depends on the pulsewidth of the laser pulses. An empirical scaling law of the fluence breakdown threshold as a function of the pulsewidth is given by $F_{th} \alpha \sqrt{\tau_p}$, or alternatively, the intensity breakdown threshold, $I_{th} = F_{th}/\tau_p$. Although this scaling law applies in the pulsewidth regime from nanosecond to tens of picoseconds, recently, we found that the breakdown threshold does not follow the scaling law when laser pulses are shorter than ten picoseconds for SiO_2 [4]. Therefore, a systematic investigation of the breakdown threshold of cornea tissue as a function of the laser pulsewidth should enable us to identify the best operating parameters.

We performed a series of experiments to determine the breakdown threshold of cornea as a function of laser pulsewidth between 150 fs - 7 ns, using a CPA laser system . One advantage of this laser system is the laser pulsewidth can be varied while all other experimental parameters (spot size, wavelength, energy, etc.) remain unchanged. The laser was focused to a spot size (FWHM) of 26 μm. The plasma emission was recorded as a function of pulse energy in order to determine the tissue damage threshold. Histology was also performed to assess tissue damage.

Breakdown thresholds calculated from plasma emission data revealed deviations from the scaling law, $F_{th} \alpha \sqrt{\tau_p}$. As shown in Figure 1, the scaling law of the fluence threshold is true to about 10 ps, and fails when the pulse shortens to less than a few picoseconds. The standard deviation of breakdown threshold measurements decreased with shorter pulses. Histological analysis reveals more localized ablation with pulses less than 10 ps.

The breakdown threshold for ultrashort pulses (< 10 ps) are less than longer pulses and have smaller standard deviations. The reduced collateral damage caused by ultrashort laser pulses show that these systems may have a future in ophthalmic and other precision surgical procedures.

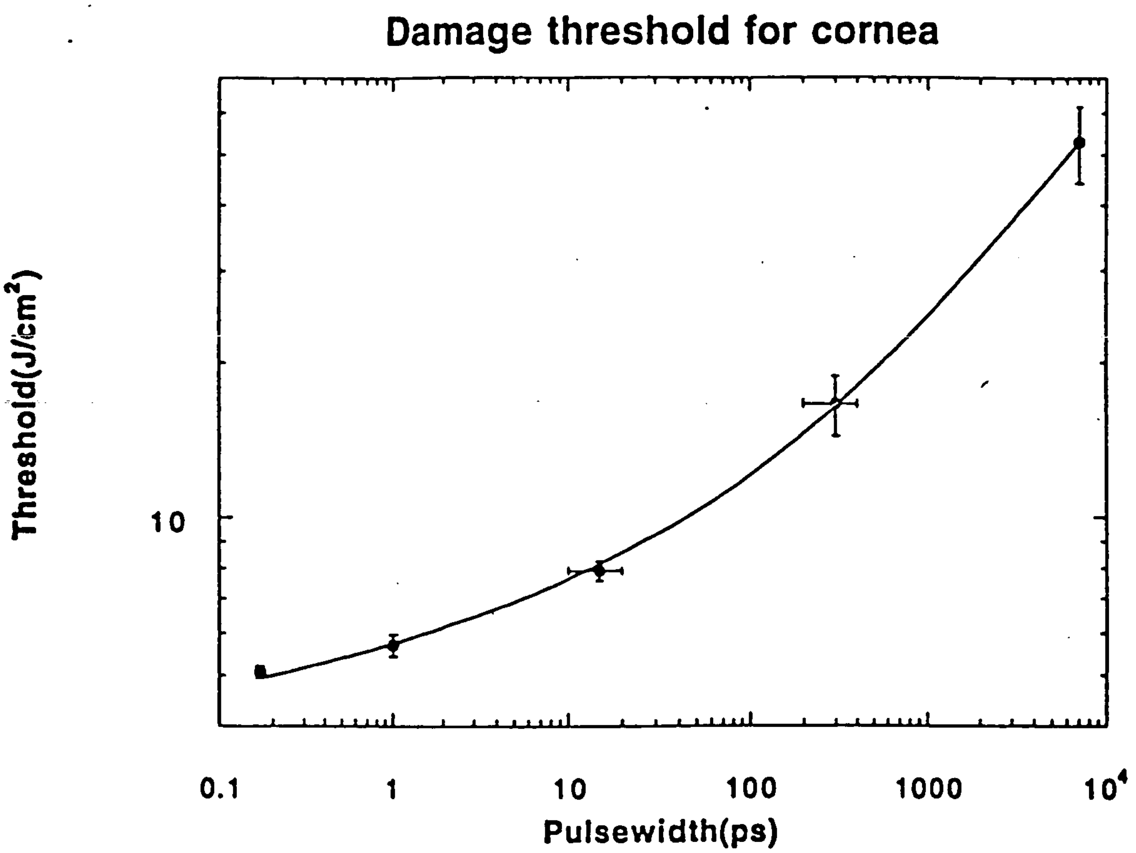


Figure 1. Damage threshold of cornea as a function of pulse duration.

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[1] J. Squier, F. Salin, G. Mourou, Opt. Lett. **16**, 324

[2] D. Stern, R. Schoenkin, C. Puliafito, E. Dobi, R. Birngraber, J. Fujimoto, Arch. Opthalmol. **107**, 587 (1987)

[3] R. Birngruber, C. Puliafito, A. Gawande, W. Lin, R. Schoenlein, J. Fujimoto, IEEE J. Quantum Electron. **23**, 1836 (1987)

[4] D. Du, X. Liu, G. Korn, J. Squier, G. Mourou, submitted to App. Phys. Lett..

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EXHIBIT 2

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BARNES, KISSELLE, RAISCH, CHOATE, WHITTEMORE & HULBERT, P.C.

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3500 PENOBSCOT BUILDING

645 GRISWOLD STREET

DETROIT, MICHIGAN 48226-4217

TELEPHONE (313) 962-4790

TELEFAX (313) 962-0168

BASIL C. FOUSSIANES
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WILLIAM J. WAUGAMAN
CHESTER L. DAVIS, JR.
WILLIAM M. FRANCIS
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OF COUNSEL
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1885-1960

JOHN M. KISSELLE
1894-1980

ARTHUR RAISCH
1902-1991

March 31, 1994

<u>VIA FACSIMILE MACHINE</u>

Mitchell A. Goodkin, Esq., P.E.
Associate Intellectual
Property Counsel
The University of Michigan
Wolverine Tower, Room 2071
3003 S. State Street
Ann Arbor, MI 48109-1280

Fax No: (313) 936-1330

Re: 939

Dear Mitch:

I am enclosing a rough draft of the proposed patent application based on the disclosure we received on [redacted] As currently constituted the application covers the various embodiments discussed with you and with the various inventors. I would appreciate it if you would coordinate obtaining review of this proposed draft or advise me as to how you would otherwise like to have this review procedure handled. It is my understanding that one of the inventors, Peter Pronko, may still be in town today so it may be possible to get a draft to him before he leaves.

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Mitchell A. Goodkin, Esq., P.E.
March 31, 1994
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I look forward to receiving your thoughts and comments on the enclosed material along with comments from the inventors.

Very truly yours,

L. Deschere

Linda Deschere
Robert Collins
Barnes, Kisselle et al

LD/sc

Enclosures